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THE SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF A CADMIUM-NITRITE COMPLEX

A THESIS

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By

Edwin G. Vassian

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OF THE DISSOCIATION CONSTANT OF A CADMIUM-NITRITE COMPLEX

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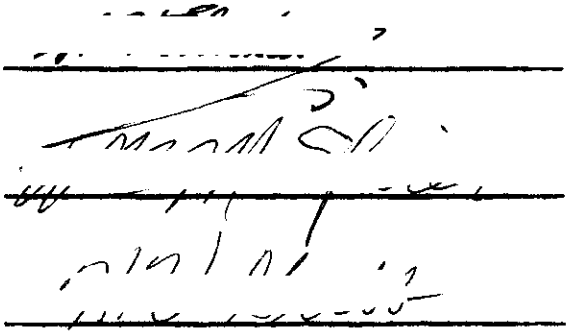

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LIST OF SYMBOLS

e	molar extinction coefficient $/cm^{-1}$ (Mole/L)$^{-1}$
D	optical density or absorbency
x	cadmium-nitrite complex
C	concentration in moles per liter
C^o	initial concentration in moles per liter
l	absorption-cell length in cm.
K	dissociation constant
u	ionic strength

ABSTRACT

Spectrophotometric observations on mixtures of cadmium and nitrite ion, at definite pH values, give strong indication of the formation of a complex or complexes between the cadmium and nitrite ions. By keeping the nitrite ion concentration constant around 0.02F, and gradually increasing the concentration of cadmium ion, it was found that the wavelength of maximum absorption of the solutions of cadmium and nitrite ions shifted from 355 mu, which is the wavelength of maximum absorption for nitrite ion alone, to 320 mu for solutions of high concentration in cadmium ion. The occurrence of an isosbestic point at 337 mu gives strong indication that only one complex is being formed between the cadmium and nitrite ions.

In order to determine the formula and dissociation constant of this complex, solutions of cadmium perchlorate and potassium nitrite were studied over a limited range of concentration at various pH values. These solutions were maintained at an ionic strength of unity by the addition of sodium perchlorate. It was shown that the perchlorate ion does not complex appreciably with cadmium ion. In reducing these data, a formula, $Cd(NO_2)_n^{2-n}$, was assumed for the complex and an attempt was made to find a single dissociation constant which would be essentially independent of the cadmium ion formality. The data support a formula $Cd(NO_2)^+$ with a dissociation constant

of 1.4×10^{-2}. Values of n greater than two are completely unsatisfactory but some support can be given for n equal to two. The method of continuous variations suggested by Job was employed to confirm the formula of the complex. Although the technique, employed in this investigation, is not entirely unequivocal, it lends strong support to the value of n equal to one.

In this study, it was necessary to consider the equilibrium:

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

since the solutions observed spectrophotometrically were maintained at low pH values in order to prevent the hydrolysis of the cadmium ion in aqueous medium. The dissociation constant of nitrous acid at an ionic strength of unity was determined to be 15.9×10^{-4}. The ionic strength of unity was obtained by the addition of sodium perchlorate to the buffered solutions of potassium nitrite. At an ionic strength of 0.07, the dissociation constant of nitrous acid was found to be 5.15×10^{-4}, which is essentially in agreement with the value reported in the literature.

Enough information was obtained on the cadmium, chloride, and nitrite ion systems to make an approximate calculation of the dissociation constant of a possible cadmium-chloride complex. It was assumed that only one cadmium-chloride complex was formed of the formula $CdCl^+$. The dissociation constant of this complex is calculated to be in

reasonable agreement with the value given in the literature.

Solutions containing several other cations, each separately mixed with the nitrite ion, were examined to determine if any indication of complex formation existed. Rubidium, cesium, magnesium, and calcium ions were separately mixed with nitrite ion but their spectra gave little indication of complex formation. Mercury and zinc were also separately mixed with nitrite ion and spectrophotometric observations of these solutions gave strong evidence of complex formation.

CHAPTER I

INTRODUCTION

The ultimate purpose of this investigation is the determination of the molecular formulae and dissociation constants of complex ions formed by the union of various cations and the nitrite ion. The general method of experimental procedure used in attempting to collect data for such a determination is to prepare solutions of known formality of the cation and nitrite ion, at a known pH, and then to observe the absorption spectrum of the solution.

The knowledge that the nitrite ion absorbs in the ultra-violet region provided a stimulus for this investigation. It was thought that if the nitrite ion could be complexed with some cation, a spectrophotometric observation of the resulting complex would result in obtaining sufficient experimental data for the determination of the molecular formula and the dissociation constant. It was thought that if this determination proved successful, it might indicate a different method of investigating the molecular formulae and dissociation constants of a certain class of complex ions.

In this study, water solutions containing a low concentration of the ions under observation were used. Some of the equilibria that were taken under consideration were:

$$H^{+} + NO_2^- \rightleftharpoons HNO_2 \qquad (1)$$

$$M^{+2} + nNO_2^- \rightleftharpoons M(NO_2)_n^{2-n} \qquad (2)$$

$$M^{+2} + mX^- \rightleftharpoons MX_m^{2-m} \qquad (3)$$

$$M^{+2} + pOH^- \rightleftharpoons M(OH)_p^{2-p} \qquad (4)$$

Where: M = Group IIB cation
X = Halide ion

Equilibrium 1 must be considered since this equilibrium will always be present as long as some nitrite ion remains in solution. Equilibrium 2 is the one that is under investigation. Equilibrium 3 was taken into consideration since it is known that the halides of Group II_B, particularly those of cadmium and mercury, are not completely dissociated in solution. The halides of these salts provide a readily available soluble salt that does not absorb appreciably in the ultra-violet region. Equilibrium 4 was taken into consideration since in an aqueous medium, there will always be a certain amount of hydroxyl ion present and thus the possibility that this equilibrium exists.

It becomes necessary, when calculating the dissociation constant of a cation-nitrite complex, to know the dissociation constant of nitrous acid at the same temperature and ionic strength at which the solution of the complex was observed. The first part of this investigation is concerned with the determination of the dissociation constant of nitrous acid at 25°C and particularly in a solution whose ionic strength is about unity. A literature search revealed that

no previous investigator has reported the dissociation constant of nitrous acid under such conditions of temperature and ionic strength. One of the few determinations reported in the literature on the dissociation constant of nitrous acid at a temperature of 25°C, but at a low ionic strength, was made by H. Schmid, R. Marchgraber, and F. Dunkl (1). By utilizing conductivity measurements on solutions of sodium nitrite and hydrochloric acid, these investigators reported a dissociation constant of 5.1×10^{-4} for nitrous acid at 25°C.

The second part of this thesis will be concerned primarily with the determination of the dissociation constant of a cadmium-nitrite complex. Evidence will then be shown that the zinc and mercuric cations also complex with the nitrite ion in aqueous solution. It is believed that the dissociation constants of these zinc-nitrite and mercuric-nitrite complexes may be determined in a manner similar to the one that will be shown for the determination of the cadmium-nitrite complex.

CHAPTER II

DETERMINATION OF THE DISSOCIATION CONSTANT OF NITROUS ACID

Basic considerations.--The spectral region in which all solutions in this thesis were studied was between 250 and 380 millimicrons (mu). This range corresponds to the near ultraviolet region where absorption of a quantum of light is dependent upon electronic transitions within the absorbing molecule. The relation, known as the Beer-Lambert law, which forms the basis for obtaining quantitative information from spectrophotometric data is:

$$\lg_{10} \frac{I}{I_o} = ecl \qquad (1)$$

Where: $I_o(x)$ = energy of wavelength, x, transmitted by a cell of thickness, l, containing pure solvent.

$I_{(x)}$ = energy of wavelength, x, transmitted by solution in a similar cell of the same length, l.

c = concentration of solution in moles per liter.

e = molar extinction coefficient which is characteristic of the absorbing medium and is a function of the wavelength.

Two other quantities have been defined which can be used to put 1 in a more convenient form. The ratio, I/I_o is defined as the "transmittancy" T, of the solution, and $-\lg_{10}T$ is known as the "optical density" or "absorbency" of the solution. Thus, 1 can be written as

$$D = ecl \qquad (2)$$

The optical density is the quantity that is recorded directly from the spectrophotometer. It can be seen from 2 that a large value of "e" for a particular substance at a given wavelength indicates a strong absorber and, conversely, a small value of "e" indicates a weak absorber.

Relation 2 is the expression for a single absorbing species. If more than one absorber is present, the resultant absorbency is the sum of the individual optical density of each active species present and equation 2, in the more general case, would be written as

$$D = e_1c_1l + e_2c_2l + \ldots + e_nc_nl \qquad (3)$$

where the subscripts refer to the various substances present.

Relation 3 may be regarded as the formulation from which quantitative information is derived from the spectrophotometer.

Relation 1 was derived on the assumption that the molar extinction coefficient, e, does not vary with a change in concentration of the absorbing species. Changes in concentration may lead to changes in the nature of the molecular species in solution. Such changes include polymer

formation and the formation of other kinds of molecular associations and also dissociation. If such changes take place, the optical density will no longer vary linearly with the concentration of the absorbing species and deviations from relation 2 will be observed.

The principle piece of equipment used in this investigation was a Beckman D. U. quartz apectrophotometer with a photomultiplier attachment. A temperature control unit was placed on one side of the cell compartment. It consisted of a flat, metal plate with grooves bored in its center such that water could be circulated through its interior when the plate was attached to a water pump with a thermostat regulator. In this manner, the temperature of the liquids in the absorption cells could be maintained within $\pm$ 0.1 of a degree centigrade of the desired temperature. The light source used on this instrument was a hydrogen discharge lamp.

The silica absorption cells were examined for variations in optical density at various wavelengths by filling both cells with distilled water and then observing deviations in the light transmitted at different wavelengths in the range 260-380 mu. No significant difference between the two cells was observed. The cells were 1.001 and 1.004 cm. in length and henceforth, the number 1 will be considered to be 1.000 cm. for all calculations. This assumption will introduce a negligible error in the calculations to be reported.

The pH of all solutions was determined by utilizing a Beckman pH meter which was standardized with a standard buffer solution which was certified to have a pH of 7.00. Readings are reliable to within 0.1 of a pH unit.

Derivation of formulae.--The calculations that are used to determine the dissociation constant of nitrous acid in this thesis require that observations be made on two separate solutions of nitrite ion at different pH values or different initial concentrations of nitrite ion or both. Three independent relationships are known from which six independent equations can be written. The classical dissociation constant in terms of concentrations will be evaluated.

The three independent relationships are:

$$C^o = C_{HNO_2} + C_{NO_2^-} \qquad (4)$$

C = concentration

C^o = initial concentration of nitrite ion

C_{HNO_2} = concentration of nitrous acid

$C_{NO_2^-}$ = concentration of nitrite ion

$$D = e_{HNO_2} C_{HNO_2} l + e_{NO_2^-} C_{NO_2^-} l \qquad (5)$$

e = molar extinction coefficient at a given wavelength

D = optical density at a given wavelength

$$K_{HNO_2} = \frac{C_H + C_{NO_2^-}}{C_{HNO_2}} \qquad (6)$$

K_{HNO_2} is dissociation constant of nitrous acid at a given ionic strength

Equations 4, 5 and 6 apply to both solutions observed. Subscripts 1 and 2 in the following equations are used to distinguish one solution from the other. All spectrophotometric observations were made at a wavelength of 358 mu. From equations 4, 5 and 6, we can write for each of the two solutions the following relationships:

$$e_{HNO_2} C_{1,HNO_2}{}^{1} + e_{NO_2^-} C_{1NO_2^-}{}^{1} = D_1 \qquad (7)$$

$$e_{HNO_2} C_{2HNO_2}{}^{1} + e_{NO_2^-} C_{2NO_2^-}{}^{1} = D_2 \qquad (8)$$

$$C_{1HNO_2} + C_{1NO_2^-} = C^{o}_{1NO_2^-} \qquad (9)$$

$$C_{2HNO_2} + C_{2NO_2^-} = C^{o}_{2NO_2^-} \qquad (10)$$

$$K_1 = \frac{C_{1H^+} C_{1NO_2^-}}{C_{1HNO_2}} \qquad (11)$$

$$K_2 = \frac{C_{2H^+} C_{2NO_2^-}}{C_{2HNO_2}} \qquad (12)$$

Let us assume that $C^{o}_{1NO_2^-} = C^{o}_{2NO_2} = C^{o}$ and that $K_1 = K_2$.

Solving equations 9 and 10 for $C_{1NO_2^-}$ and $C_{2NO_2^-}$ respectively, and substituting back into (7) and (8), we obtain:

$$e_{HNO_2} C_{1NO_2}{}^{1} + e_{NO_2^-} (C^{o}-C_{1HNO_2})1 = D_1 \qquad (13)$$

$$e_{HNO_2} C_{2HNO_2}{}^{1} + e_{NO_2^-} (C^{o}-C_{2HNO_2})1 = D_2 \qquad (14)$$

Solving (13) and (14) for e_{HNO_2} and equating, we obtain

$$\frac{D_1 - e_{NO_2^-} (C^o - C_{1HNO_2})1}{C_{1HNO_2}} = \frac{D_2 - e_{NO_2^-} (C^o - C_{2HNO_2})1}{C_{2HNO_2}} \quad (15)$$

By rearranging terms in (15) and solving for C_{2HNO_2}/ C_{1HNO_2} we obtain

$$\frac{C_{2HNO_2}}{C_{1HNO_2}} = \frac{D_2 - e_{NO_2^-} C^o 1}{D_1 - e_{NO_2^-} C^o 1} = B \quad (16)$$

Remembering that $K_1 = K_2$, we next divide equation 11 by equation 12 and obtain:

$$1 = \frac{C_{2HNO_2}}{C_{1HNO_2}} \cdot \frac{C_{1NO_2^-}}{C_{2NO_2^-}} \cdot \frac{C_{1H^+}}{C_{2H^+}} \quad (17)$$

Substituting (16) into (17) and solving for $C_{2NO_2^-}$, we have

$$C_{2NO_2^-} = B\, C_{1NO_2^-} \cdot \frac{C_{1H^+}}{C_{2H^+}} \quad (18)$$

Substituting (16) and (18) into (10), we obtain

$$B\, C_{1HNO_2} + B\, C_{1NO_2^-} \frac{C_{1H^+}}{C_{2H^+}} = C^o \quad (19)$$

Solving (19) and (9) for C_{1HNO_2} we have

$$C_{1HNO_2} = \frac{C^o \left(1 - B \frac{C_{1H^+}}{C_{2H^+}}\right)}{B \left(1 - \frac{C_{1H^+}}{C_{2H^+}}\right)} \quad (20)$$

If the initial concentrations of nitrite ion are not the same in the two solutions under consideration, then we obtain for equation (16) by the same reasoning:

$$\frac{D_2 - e_{NO_2^-} C_2^o 1}{D_1 - e_{NO_2^-} C_1^o 1} = B' \qquad (21)$$

from which is finally derived an expression similar to (20 which is:

$$C_{1HNO_2} = \frac{C^o_{2NO_2^-} - B' C^o_{1NO_2^-} \frac{C_{1H'}}{C_{2H'}}}{B'\left(1 - \frac{C_{1H'}}{C_{2H'}}\right)} \qquad (22)$$

Experimental data.--Observations were made on several different solutions of nitrite ion buffered at various pH values. The data of these solutions is summarized in table 1.

TABLE 1

Optical Density of Solutions of Nitrite Ion at Various pH Values

Solution	pH	$C_{H'}$	D_{358mu}	$C^o_{NO_2^-}$	u
(1)	4.55	2.82×10^{-5}	0.530	0.02257	0.06
(2)	3.23	5.59×10^{-4}	0.798	0.02257	0.07
(3)	3.20	6.33×10^{-4}	0.840	0.02302	0.07
(4)	2.19	6.45×10^{-3}	1.03	0.02257	0.08
(5)	6.50	3.16×10^{-7}	0.501	0.02257	0.02

All reagents used were of C. P. grade. The potassium nitrite was analyzed by the method recommended in Kolthoff and Sandall (2). This analysis disclosed that the potassium nitrite was 95.0 per cent KNO_2. The rest was presumed to be potassium nitrate. Neither the potassium ion or the nitrate

ion absorb appreciably in the region studied.

The buffer for solutions 1 and 3 consisted of a mixture of sodium acetate and acetic acid. The buffer for 2 was made by titrating hydrochloric acid into a solution of potassium acid phthalate. The buffer solution for 4 consisted of a mixture of phosphoric acid and primary potassium phosphate. Solutions designated by 5 are unbuffered potassium nitrite and the data represent the mean of many determinations which demonstrated in addition that the solutions conform to Beer's law at this pH.

Assuming that the dissociation constant of nitrous acid is about 5×10^{-4}, the ratio of concentration of nitrous acid to that of nitrite ion at a pH of 6.50 (solution 5) is about 1 to 1600 and the nitrous acid may be neglected. Hence, these data allow the evaluation of the molar extinction coefficient of the nitrite ion which was found to be 22.2 ± 0.2 cm.$^{-1}$ (Mole/L)$^{-1}$ at 358 mu. Subsequent experiments have demonstrated that the spectrum of nitrite ion is unchanged by increasing the ionic strength to 1.00 with sodium perchlorate.

Five different combinations of the solutions listed in table 1, taken two at a time, were used to calculate K_{HNO_2}. The pair of data corresponding to solutions 2 and 3 was not used since the small difference between the pH values of these solutions introduces large errors in the calculations.

TABLE 2

Dissociation Constants Calculated for HNO_2 at 25°C

Solutions	K
(1), (2)	5.17×10^{-4}
(1), (3)	5.44
(2), (4)	5.15
(1), (4)	5.16
(3), (4)	4.87

The mean value for K_{HNO_2} (classical) from these five calculations is 5.15×10^{-4} with an estimated standard deviation of $\pm 0.2 \times 10^{-4}$

The value for e_{HNO_2} was obtained by solving equation 5 for e_{HNO_2} and utilizing the calculations made for solutions 1 to 4. The values obtained for e_{HNO_2} are contained in table 3.

TABLE 3

Calculated Values of e_{HNO_2} at a Wavelength of 358 mu.

Solution	e_{HNO_2}
(1)	47.0
(2)	47.6
(3)	47.1
(4)	47.5

The arithmetic mean of e_{HNO_2} is 47.3 ± 0.3 $cm^{-1}(Mole/L)^{-1}$

Determination of the Dissociation constant at unit ionic strength.--The solutions that were observed in the determination of the dissociation constant of the cadmium-nitrite

complex were maintained at an ionic strength of unity. Since the dissociation constant of nitrous acid is involved in the calculation of the dissociation constant of the cadmium-nitrite complex, it became necessary to determine the dissociation constant of nitrous acid at an ionic strength of unity.

A solution that was 0.02257F in potassium nitrite and had a pH of 3.25 and an ionic strength of 1.00 was prepared by mixing solutions of potassium nitrite and potassium acid phthalate--hydrochloric acid buffer with enough sodium perchlorate solution to bring the ionic strength of the resultant solution up to 1.00. This solution was observed at 358 mu. Another control solution was prepared in exactly the same manner as the one just described except that no sodium perchlorate solution was added. The ionic strength of this second solution was 0.06.

The derivation of the formulae used in these calculations is as follows: Equations 4 and 5 were solved for $C_{NO_2^-}$ and we obtain:

$$C_{NO_2^-} = \frac{e_{HNO_2^-}\ C^o_{NO_2^-} l - D}{e_{HNO_2} - e_{NO_2}} \qquad (23)$$

Equations 23 and 4 were then used to obtain $C_{NO_2^-}$ and $C_{HNO_2^-}$ respectively, using the values of $e_{NO_2^-}$ and e_{HNO_2} determined from the study at low ionic strength. The C_{H^+} is known from the pH of the solution. The dissociation constant of nitrous acid was calculated at the two different ionic

strengths. The results are contained in table 4.

TABLE 4

Dissociation Constants Calculated for Nitrous Acid at Low and High Ionic Strengths

$C^{o}_{NO_2^-}$	pH	u	D	K_{HNO_2}
0.02257	3.25	1.00	0.650	15.9×10^{-4}
0.02257	3.25	0.06	0.770	5.95×10^{-4}

Summary.--The important results of this study are the determination of the following quantities.

(1) $e_{NO_2^-}$ at a wavelength of 358 mu = 22.2 $\pm$ 0.2 cm^{-1} (Mole/L)

(2) e_{HNO_2} at a wavelength of 358 mu = 47.3 $\pm$ 0.3 cm^{-1}

(3) K_{HNO_2} at ionic strength of 0.07 = 5.15×10^{-4}

(4) K_{HNO_2} at ionic strength of 1.00 = 15.9×10^{-4}

The ionization constants are believed reliable to within $\pm$ 5 per cent.

CHAPTER III

DETERMINATION OF THE DISSOCIATION CONSTANT OF CADMIUM ION COMPLEXING WITH NITRITE ION

The belief that a complex or complexes are formed when cadmium ion and nitrite ion are in aqueous solution together was based on the differences between the absorption spectrum of mixtures of these two ions and the spectra of the two ions separately. The spectrum of nitrite ion, in the spectral range 260-380 mu. is well known. Solutions of cadmium chloride in this spectral range did not show any appreciable absorption. Therefore, the variation in the spectrum of a solution of nitrite ion upon the addition of cadmium ion was attributed to the formation of a complex or complexes between the cadmium ion and nitrite ion. Fig. 1 shows graphically the results obtained from the study of solutions having a constant formality of 0.0221 in potassium nitrite but varying concentrations of cadmium chloride. The cadmium concentration varied from 0.0000200F to 2.00F. The pH of all solutions was about 6.0.

Graph 2 in Fig. 1 is the curve obtained when the solution was 0.0000200F in cadmium ion. This solution has the same absorption maximum as nitrite ion alone and exhibits almost the same degree of absorption at each wavelength. As the cadmium ion concentration is increase, the absorption

Figure 1. The Absorption Spectra of Solutions Containing a Fixed Amount of Nitrite Ion with Varying Amounts of Cadmium Ion.

maximum decreases until a minimum point is reached and then increases again. Graph 70, Fig. 1 represents the data obtained from the solution that was 2.00F in cadmium ion. This solution had the highest concentration of cadmium in this series of observations.

An inspection of the curves plotted in Fig. 1 lead to the belief that only a single complex is being formed. This belief is based on the occurrence of an isosbestic point at 337 mu. where all the curves intersect. Such an intersection implies either the existence of only two species containing the nitrite ion or a fortuitously identical molar extinction coefficient at the isosbestic wavelength for two different species. Since the latter possibility seems unlikely, it will be assumed that only one complex ion containing the nitrite and cadmium ions exists in solutions in the range of the nitrite ion concentration studied.

All measurements in the determination of the dissociation constant of the complex ion were made at 25°C.

Measurements with cadmium chloride and cadmium perchlorate.--It is known that cadmium ion and chloride ion form a series of complexes in aqueous solution ranging from $CdCl^{+}$ to $CdCl_3^-$ (3). In order to avoid complications resulting from these equilibria in the determination of the dissociation constant of the cadmium-nitrite complex, the cadmium ion was introduced into solution in the form of cadmium perchlorate.

To be certain that a cadmium-perchlorate complex was not being formed in solution, the following experiments were performed on solutions 0.0500F in cadmium chloride and 0.0221F in potassium nitrite and having a pH of 5.50. The maximum absorption band for this solution occurred at 320 mu. Another solution with the same pH and containing the same concentrations of cadmium and nitrite ion but also 1.00F in sodium chloride was observed and exhibited a maximum absorption at 350 mu. A third solution having the same pH and concentrations of cadmium and nitrite ion as the first two solutions, but also being 1.00F in sodium perchlorate, was observed. Its maximum absorption occurred at 320 mu. Eivdently, the additional chloride ion in the second solution shifted the equilibrium to favor the cadmium chloride complexes and caused the absorption maximum to occur much closer to that observed for nitrite ion alone. The fact that no such shift in absorption maximum was observed for the solution with additional perchlorate ion indicates that no appreciable shift in the equilibrium between cadmium and nitrite ions is caused by the presence of perchlorate ions and hence suggests the use of perchlorates for the addition of cadmium ion and for the adjustment of ionic strength.

Reagents.--The cadmium chloride used was Baker's C. P., anhydrous. A stock, aqueous solution of this salt was pre pared and analyzed for cadmium content by precipitation of

the chloride ion using silver nitrate. The solutions used in the study of the complex were prepared by dilution of this stock solution.

The cadmium perchlorate was prepared as follows: cadmium carbonate, Baker's C. P., was placed in a beaker containing enough water to make a thin slurry. Perchloric acid, Baker's, 70-72 per cent, was added, slowly, with constant stirring until a clear solution was obtained. The solution was then heated to the boiling point and maintained at that temperature during the rest of the procedure. More cadmium carbonate was added followed by enough perchloric acid to obtain a clear solution. This process was repeated until the cadmium perchlorate was approximately 2.00F. Some excess cadmium carbonate was then added and the solution allowed to stand overnight. It was then filtered four times until a clear liquid was obtained. This solution was analyzed for the cadmium content by pipetting a measured volume into a platinum crucible, adding several ml. of 9.0F H_2SO_4 and evaporating to dryness on a hot plate. The crucible was then maintained in an oven at 500°C for one hour, cooled, and thd contents weighed as cadmium sulphate.

The sodium perchlorate was prepared by neutralizing an aqueous solution of sodium hydroxide, Fischer's C. P., with perchloric acid until a pH of 6.60 was obtained.

Equilibria considered.--The various species and equilibria may be described as follows: the reagents used in the

determination of the equilibrium constant of the cadmium-nitrite complex were potassium nitrite, cadmium perchlorate, sodium perchlorate, and perchloric acid, all dissolved in an aqueous medium. The various ions present in solution are potassium, nitrite, cadmium, perchlorate, hydrogen, and hydroxyl ions. Some equilibria that may be present are:

$$Cd^{++} + nNO_2^- \rightleftharpoons Cd(NO_2)_n^{2-n} \quad (1)$$

$$Cd^{++} + pOH^- \rightleftharpoons Cd(OH)_p^{2-p} \quad (2)$$

$$Cd^{++} + qClO_4^- \rightleftharpoons Cd(ClO_4)_q^{2-q} \quad (3)$$

$$H^+ + NO_2^- \rightleftharpoons HNO_2 \quad (4)$$

It is assumed that no equilibria exist between the potassium and any anion and that hydrogen ion in equilibrium with hydroxyl ion can be neglected. Equilibrium 1 is the system for which this investigation was principally undertaken. The pH of all systems observed was sufficiently low as to make the existence of 2 improbable. Furthermore, studies at different pH levels in the range from 3.30 to 3.90 may be interpreted consistently without introducing this equilibrium. The presence of 3 was shown to be negligible. Equilibrium 4 was taken into consideration in all calculations involving the dissociation constant of the cadmium-nitrite complex.

Determination of the Extinction Coefficient of the Cadmium-Nitrite Complex.--In order to determine the molar extinction coefficient of the cadmium-nitrite complex, a solution con-

taining a definite formality of nitrite ion and a relatively high concentration of cadmium ion was prepared. It was assumed that at these relative concentrations of nitrite and cadmium ions, the absorption observed would be due almost entirely to the cadmium-nitrite complex. The data obtained from this experiment at 25°C is contained in table 5 where $C^{o}_{Cd^{++}}$ is the formality of $Cd(ClO_4)_2$, $C^{o}NO_2$ that of KNO_2. The pH was adjusted with $HClO_4$ and D is the optical density measured at 320 mu.

TABLE 5

Optical Density of Solutions Containing a High Ratio of Cadmium to Nitrite Ions

Solution	$C^{o}_{Cd^{++}}$	$C^{o}NO_2^-$	pH	D
(1)	0.568	0.0230	4.10	0.600
(2)	2.50	0.0115	4.10	0.300

The above data provides additional support for the assumption that there is only one absorbing complex ion in solutions 1 and 2. Since increasing the relative concentration of cadmium ion by a factor of approximately ten in solution 2 has produced no proportional change in absorption by this solution, it is assumed, therefore, that the possible equilibrium:

$$Cd^{++} + nNO_2^- \rightleftharpoons Cd(NO_2)_n^{2-n}$$

has been driven almost to completion towards the right by having a large excess of cadmium ion in solution.

The absorption coefficient for the complex was calculated in the usual manner as follows:

$$D_x = e_x C_x 1$$

$$e_x = \frac{D_x}{C_x 1}$$

But $C_x = C^o_{NO_2^-}/n$ and $1 = 1.00$ cm. Therefore

$$e_x = \frac{nD}{C^o_{NO_2}}$$

Utilizing the data from solution 2, we have

$$e_x = \frac{n(0.300)}{0.0115} = n26.1,$$

which is identical with the value obtained from data on solution 1.

Experimental data.--In order to evaluate n and determine the dissociation constant of the cadmium-nitrite complex formed, solutions of known initial formality in nitrite ion and cadmium ion were prepared. The pH of each solution was determined after addition of perchloric acid. The ionic strength was maintained at unity in all solutions by the addition of sodium perchlorate. The data obtained are presented in table 6.

TABLE 6

Optical Densities of Solutions of Cadmium and Nitrite Ions Observed at the Wavelength of Maximum Absorption of the Complex, 320 mu.

Solution	C^{o}_{Cd}	$C^{o}_{NO_2}$	pH	D_{320}
(1)	0.2128	0.02302	3.90	0.540
(2)	0.2128	0.02302	3.90	0.530
(3)	0.0532	0.02302	3.90	0.450
(4)	0.0532	0.02302	3.30	0.400
(5)	0.01064	0.02302	3.90	0.330
(6)	0.01064	0.02302	3.30	0.320
(7)	0.01064	0.01151	3.90	0.175
(8)	0.01064	0.01151	3.30	0.151

Derivation of formulae.--Five independent relationships for the evaluation of the data obtained by spectrophotometric measurements were used. They are:

$$D = e_{NO_2^-} C_{NO_2} l + e_{HNO_2} C_{HNO_2} l + e_x C_x l \qquad (24)$$

$$C^{o}_{NO_2} = C_{NO_2} + C_{HNO_2} + nC_x \qquad (25)$$

$$C^{o}_{Cd} = C_{Cd^{++}} + C_x \qquad (26)$$

$$K_{HNO_2} = \frac{C_{H^+} C_{NO_2^-}}{C_{HNO_2}} \qquad (6)$$

$$K = \frac{C_{Cd} C^{n}_{NO_2^-}}{C_x} \qquad (27)$$

Equation 24 assumes that there are only three absorbing species in solution and evidence has been given that each of these species absorbs considerably in the region investigated. Equation 25 assumes that there are only two equilibria

present in solution and that only one complex of cadmium-nitrite is formed. Evidence has been shown that these are justifiable assumptions. Equations 26, 6 and 27 assume, along with 25, that there are only two equilibria present in solutions, namely

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

and

$$Cd(NO_2)_n^{2-n} \rightleftharpoons Cd^{++} + nNO_2^-$$

Equation 27 also assumes that an equilibrium constant does exist for the cadmium-nitrite complex.

Solving 24 and 25 for C_x, we obtain equations 28 and 29, respectively

$$C_x = \frac{D - e_{NO_2^-} C_{NO_2^-} l - e_{HNO_2} C_{HNO_2} l}{e_x l} \qquad (28)$$

$$C_x = \frac{C^o_{NO_2^-} - C_{NO_2^-} - C_{HNO_2}}{n} \qquad (29)$$

Equating equations 28 and 29, we obtain

$$\frac{D - e_{NO_2^-} - C_{NO_2^-} l - e_{HNO_2} C_{HNO_2} l}{e_x l} = \frac{C^o_{NO_2^-} - C_{NO_2^-} - C_{HNO_2}}{n} \qquad (30)$$

Solving 6 for C_{HNO_2}, and letting $A = \frac{C_{H^+}}{K_{HNO_2}}$

we have

$$C_{HNO_2} = AC_{NO_2^-}$$

Expanding 30 and substituting into it 31 and solving for $C_{NO_2^-}$, we obtain

$$C_{NO_2^-} = \frac{e_x C^o_{NO_2^-} l - nD}{e_x(l + A)l - n(e_{NO_2^-} + Ae_{HNO_2})l} \qquad (32)$$

Since the value of e_{HNO_2} is not easily determined by experiment because of the instability of nitrous acid at high concentrations, the quantity, $e_{NO_2^-} + A\, e_{HNO_2}$, which appears in 32 was determined by observing solutions of nitrite ion, alone, at definite pH values. The data obtained for the calculation of e_{HNO_2} is listed in table 7.

TABLE 7

Optical Densities of Solutions of Nitrite Ion, Alone, at Various pH Values

$C^o_{NO_2^-}$	D^o(pH=3.30)	D^o(pH=3.90)	D^o(pH=4.90)
0.02302	0.255	0.256	0.265

D^o is the optical density of a solution containing only the nitrite ion at a definite pH value. The calculation of $e_{HNO_2} + Ae_{NO_2^-}$ was based on the following argument: assuming that the only absorbing species in a solution of nitrite ion are the nitrite ion, itself, and nitrous acid, we have from equation 5

$$D^o = e_{NO_2^-} C_{NO_2^-} l + e_{HNO_2}\, C_{HNO_2} l \qquad (5\text{-}1)$$

Substituting (31) into (5-1), we obtain

$$D^o = C_{NO_2^-}\, (e_{NO_2^-} + Ae_{HNO_2})l \qquad (33)$$

Substituting 31 into 4 and solving for $C_{NO_2^-}$, we have

$$e_{NO_2^-} \not\propto Ae_{HNO_2} = \frac{D^o(1 \not\propto A)}{C^o_{NO_2^-}} \qquad (35)$$

Thus, from the D^o values in table 9 and 35, we obtain the value of $e_{NO_2} \not\propto Ae_{HNO_2}$. Knowing this value, the quantity e_{HNO_2} can be easily solved. These calculations are presented in table 8.

TABLE 8

Calculated Values for Molar Extinction Coefficient of Nitrous Acid at 320 mu.

pH	$e_{NO_2^-} \not\propto Ae_{HNO_2}$	e_{HNO_2}
3.30	25.4	11.4
3.90	14.6	11.5
4.90	11.9	22.4

The value of e_{HNO_2} at the pH of 4.90 was rejected since the calculations at this pH were thought to be the least reliable due to the ratio of about 1:40 of nitrous acid to nitrite ion at this pH.

Discussion of results.--The experimental data from table 6 was used to determine the number of complexing nitrite ions per cadmium ion and the dissociation constant of the complex formed. It was expected that if the data in table 6 was evaluated by the use of equations 25, 26, 27, 31 and 32 by

assuming different integral values for n, the correct selection of n would lead to the evaluation of a series of numbers, i.e., dissociation constants, that would vary little from one another in magnitude. However, the dissociation constants calculated in on the basis of the other n values would show a distinct drift as the ratio of the concentrations of cadmium ion to nitrite ion changed with each successive solution. The results of these calculations are presented in table 9. It seems immediately evident that the number of complexing nitrite ions per cadmium ion is not equal to three or four. It was assumed that selections of n greater than four would lead to results similar to those found for n equal to three or four. However, difficulty is encountered when an attempt is made to make a selection of n on the basis of n equal to one or two. If the value of n had to be selected on the basis of these calculations alone, it would appear more likely to select n equal to one since the average difference between the dissociation constant values for n equal to one are less than for n equal to two. The drift in the dissociation constant values calculated on the basis of n equal to one suggested that further investigation be made to establish the value of n.

It was thought that perhaps some of the experimental data was yielding numbers that were not sufficiently accurate for the present investigation. An inspection of equation (32) shows that there are five experimentally determined

numbers in this formulation. They are e_x, $C^o_{NO_2^-}$, D, C_{H^+}, K_{HNO_2}, and $e_{NO_2^-}$. The only number among these that could be shifted in either a plus or minus direction so as to cause the dissociation constant values, for the right selection of n, to converge, is e_x. A consistent plus or minus alteration in the other values would simply cause a displacement in the dissociation constant values for any n selected. It was thought, therefore, that there must be a more nearly correct value for e_x for n equal to either one or two. It should be impossible to find any other value of e_x that would make the dissociation constants for the incorrect selection of n converge. In calculating a new e_x for n equal to one and two, the two dissociation constants with the largest numerical difference were selected as a basis for determining the new e_x. This new e_x was then placed into the calculations for the re-determination of the other dissociation constants. An e_x of 24.6 was found for n equal to one which brought the dissociation constants for this value of n into excellent agreement. No value of e_x for n equal to two could be found that would give a similar degree of agreement. An e_x of 57.0 was found to bring the dissociation constants calculated for n equal to two into better agreement. The results of these calculations are listed in table 10.

TABLE 9

Dissociation Constants for the Cadmium-Nitrite Complex Using the Experimental Molar Extinction Coefficients

The dissociation constants in this table have been calculated with the following conditions:

$$K_{HNO_2} = 15.9 \times 10^{-4}$$

$$e_x(n) = 26.1n$$

$C^o_{Cd^{++}}$	C^o_{NO2}	pH	K (n=1)	K (n=2)	K (n=3)	K (n=4)
0.2128	0.02302	3.90	3.80×10^{-2}	2.96×10^{-4}	1.71×10^{-6}	8.75×10^{-9}
0.0532	0.02302	3.90	2.88×10^{-2}	6.20×10^{-4}	9.25×10^{-6}	1.21×10^{-7}
0.01064	0.02302	3.90	1.95×10^{-2}	9.05×10^{-4}	2.62×10^{-5}	6.70×10^{-7}
0.01064	0.01151	3.90	1.84×10^{-2}	3.46×10^{-4}	---	---
0.2128	0.02302	3.30	3.80×10^{-2}	2.86×10^{-4}	9.60×10^{-7}	4.06×10^{-9}
0.0532	0.02302	3.30	4.67×10^{-2}	10.2×10^{-4}	5.29×10^{-6}	5.62×10^{-8}
0.01064	0.02302	3.30	2.08×10^{-2}	7.86×10^{-4}	1.55×10^{-5}	2.96×10^{-6}

TABLE 10

Dissociation Constants for Cadmium-Nitrite Complex Using Adjusted Molar Extinction Coefficients

The dissociation constants in this table have been calculated with the following conditions:

$K_{HNO_2} = 15.9 \times 10^{-4}$

e (n=1) = 24.6

e (n=2) = 57.0

$C^o_{Cd^{++}}$	$C^o_{NO_2^-}$	pH	K (n=1)	K (n=2)
0.2128	0.02302	3.90	1.56×10^{-2}	9.58×10^{-4}
0.0532	0.02302	3.90	2.14×10^{-2}	10.3×10^{-4}
0.01064	0.02302	3.90	1.50×10^{-2}	12.2×10^{-4}
0.01064	0.01151	3.90	1.47×10^{-2}	4.61×10^{-4}
0.2128	0.02302	3.30	1.88×10^{-2}	7.95×10^{-4}
0.0532	0.02302	3.30	3.78×10^{-2}	15.5×10^{-4}
0.01064	0.02302	3.30	1.76×10^{-2}	11.0×10^{-4}

Determination of n by the method of continuous variations.--Job, (4), has shown a method of determining the number of ions of a particular species that complex with a different single ion if a suitable property of the solution can be measured. A property which readily lends itself to the particular problem in this investigation is a spectrophotometric measurement on the solution involved. In this method of con-

tinuous variations, equiformal solutions of the two ions that complex with each other are mixed in such proportions that the total formality remains constant. Consider the equilibrium.

$$A + nB \rightleftharpoons ABn$$

If y is the volume of solution containing B, then L-y is the volume of solution containing A and the total volume remains equal to L after mixing. A series of such solutions are made and observed on the spectrophotometer at a wavelength corresponding to maximum absorption of the complex. A plot is then made of D - xD' versus x where D is the observed optical density of the particular solution; x is the fraction y/L and D' is the absorption due to B alone. The relation, $x_{max.} = \frac{1}{n+1}$, is then used to determine n.

In this investigation, solutions 0.04604F in cadmium perchlorate and potassium nitrite were used to make the series of solutions from which measurements were made. The pH was kept constant at 4.50 and the ionic strength was maintained at 1.00 by means of sodium perchlorate. The following data was obtained.

TABLE 11

Experimental D-xD' Values at u=1.00

x	1	0.7	0.6	0.5	0.4
Ml.K_{NO_2}	30	21	18	15	12
Ml.$Cd(ClO_4)_2$	0	9	12	15	18
D	0.515	0.485	0.450	0.400	0.340
D-xD'	0	0.125	0.141	0.143	0.134

The initial solutions of potassium nitrite and cadmium perchlorate were 0.07673F and were combined to form a total volume of 30 ml. 15.8 ml. of sodium perchlorate was added to each solution which was then diluted to 50 ml. making the total formality 0.04604.

It is seen that $x_{max.}$ occurs a 0.5. According to the formula given above involving $x_{max.}$ a value of 0.5 for $x_{max.}$ corresponds to n equal to one. This same experiment, under the same conditions of concentrations of nitrite and cadmium ions but with the ionic strength maintained at 0.05, was performed in the same manner. The results are listed below.

TABLE 12

Experimental D-xD' Values at u=0.05

x	1	0.7	0.6	0.5	0.4
Ml.KNO_2	50	35	30	25	20
Ml.$Cd(ClO_4)_2$	0	15	20	25	30
D	0.515	0.507	0.460	0.410	0.335
D-xD'	0	147	151	153	129

The initial solutions of potassium nitrite and cadmium perchlorate were each 0.0460F. The total volume, after mixing, was 50 Ml so that the final formality was the same as in the experiment above, i.e., 0.04604. It is seen from table 12 that $\bullet_{max.}$ occurs at 0.50 which corresponds to n equal to one.

By using the data obtained from the method of continuous variations, it was next thought that it might be interesting to see if one could use the Kx found for n equal to one and calculate the D values obtained by experiment. One could then do the same for n equal to two and observe where $x_{max.}$ lies in each case, and the kind of correspondence obtained between the calculated and observed D values. The Kx selected for the calculations on the basis of n equal to one was 1.4×10^{-2}. The value of Kx for n equal to two was 4×10^{-4}. The basis forthe calculations is as follows:

solving 25 and 31 for $C_{NO_2^-}$, we obtain:

$$C_{NO_2^-} = \frac{C^o_{NO_2^-} - nCx}{1 + A} \qquad (36)$$

The expressions for $C_{Cd^{++}}$ and $C_{NO_2^-}$ from 26 and 36 respectively, are then substituted in the equilibrium expression for the complex

$$Kx = \frac{C_{Cd^{++}} \; C^n_{NO_2^-}}{Cx} \qquad (27)$$

Expression 27 is then solved for Cx, after which $C_{Cd^{++}}$ and $C_{NO_2^-}$ can be calculated from 26 and 36 respectively. Assuming that the nitrite ion, nitrous acid, and the complex molecule are the only absorbing species in solution, we then use relation 24 to calculate D. $e_{NO_2^-}$ and lx have been previously determined. The adjusted numbers for e_x were used. $C_{NO_2^-}$ and C_{HNO_2} were evaluated by 36 and 31 respectively. The results of these calculations are summarized in table 13.

TABLE 13

Calculated D-xD' Values for n Equal to One and Two

			n = 1			
x	1	0.8	0.7	0.6	0.5	0.4
D	0.515	0.497	0.475	0.445	0.416	0.342
D - xD'	0	0.085	0.115	0.136	0.158	0.136
			n = 2			
x	1	0.8	0.7	0.6	0.5	0.4
D	0.515	0.581	0.568	0.515	0.437	0.319
D - xD'	0	0.169	0.208	0.206	0.179	0.113

It is seen from table 13 that the maximum for n equal to one occurs at x equal to 0.5. The maximum for D - xD' for n equal to two occurs at 0.7. Thus, the experimental and calculated maximum values of D - xD' occur at the same value of x for n equal to one. It is also noticed that the differences between the experimental and calculated values of D - xD', at an ionic strength of 1.00 are much smaller for n equal to one than for n equal to two. There is thus better evidence for believing that n is equal to one rather than two.

CHAPTER IV

SUMMARY

The important results that have come out of the effort to establish the dissociation constants of the cadmium-nitrite complex are:

A cadmium-nitrite complex does exist which has a formula $CdNO_2^+$.

The dissociation constant for this complex is 1.4×10^{-2}, in a solution of ionic strength, 1.00, prepared with sodium perchlorate. The existence of complex formation between mercuric and zinc ions and the nitrite ion has strong support from spectrophotometric observations on separate solutions of mercuric and zinc ions with the nitrite ion.

APPENDIX A

ESTIMATION OF THE DISSOCIATION CONSTANT OF A CADMIUM-CHLORIDE

In the first part of this thesis, it was remarked that solutions of cadmium chloride and potassium nitrite were observed at high pH values. It has been reported that cadmium and chloride ions combine to give cadmium-chloride complexes that range from $CdCl^{+}$ to $CdCl_3^-$ (5). An attempt will be made to determine the dissociation constant of one of the cadmium-chloride complexes and to see if this value can be approximately checked in the literature. The derivation of the formulae involved are as follows:

$$D = e_{NO_2^-} C_{NO_2^-} l + e_{CdNO_2^+} C_{CdNO_2^+} l \qquad (37)$$

$$C^{o}_{Cd} = C^{++}_{Cd} + C_{CdCl^+} + C_{CdNO_2^+} \qquad (38)$$

$$C^{o}_{NO_2^-} = C_{NO_2^-} + C_{CdNO_2^+} \qquad (39)$$

$$C^{o}_{Cl^-} = C_{Cl^-} + C_{CdCl^+} \qquad (40)$$

$$K_{CdNO_2^+} = \frac{C_{Cd^{++}}\, C_{NO_2^-}}{C_{CdNO_2^-}} \qquad (27)$$

$$K_{CdCl^+} = \frac{C_{Cd^{++}}\, C_{Cl^-}}{C_{CdCl^+}} \qquad (41)$$

Equation 37 assumes that there are only two absorbing species in solution; the nitrite ion and the $CdNO_2^+$ complex. The solutions of cadmium, nitrite, and chloride ions were observed at a pH of 6.50 so that the amount of nitrous acid in solution can be neglected. Previous experiments indicate that the cadmium-chloride complex does not absorb.

Equation 38 assumes the formation of only one cadmium-chloride complex.

Solving 27 for $C_{CdNO_2^+}$, and substituting in 39, we have:

$$C_{NO_2^-} = \frac{C^o_{NO_2^-}}{1 + \frac{C_{Cd^{++}}}{K_{CdNO_2^+}}} \qquad (42)$$

Solving 27 again for $C_{CdNO_2^+}$ and substituting this resultant expression into 37, we obtain

$$D = C_{NO_2^-} (e_{NO_2^-} + e_{CdNO_2^+} \frac{C_{Cd^{++}}}{K_{CdNO_2}}$$

Substituting 41 into 42 and solving for $C_{Cd^{++}}$, we obtain

$$C_{Cd^{++}} = K_{CdNO_2^+} \frac{D - C^o_{NO_2^-} e_{NO_2^-}}{C^o_{NO_2^-} e_{CdNO_2^+} - D} \qquad (44)$$

The experimental data obtained for the determination of the cadmium-chloride complex is contained in table 14 along with the calculated dissociation constants of the cadmium-chloride complex.

TABLE 14

Dissociation Constants Calculated for the Cadmium-Chloride Complex ($CdCl^+$)

$C^o_{NO_2^-}$	$C^o_{Cd^{++}}$	$C^o_{Cl^-}$	D(320 mu.)	K_{CdCl^+}
0.02210	0.2164	0.4328	0.478	5.00×10^{-2}
0.02210	0.0541	0.1082	0.419	3.94×10^{-2}
0.02210	0.02164	0.04328	0.377	6.85×10^{-2}

The value for the dissociation constant of the cadmium monochloride complex, given in the literature is 1.1×10^{-2} which was calculated from conductance measurements (5).

APPENDIX B

COMPLEX FORMATION OF NITRITE ION WITH OTHER CATIONS

A study was made of solutions of the chlorides of a few of the alkali metals, alkaline earths, and the rest of Group II_B, containing nitrite ion to determine whether or not any indication of complex formation could be found. Rubidium, cesium, magnesium, calcium, and barium showed little indication of complex formation since the spectrum obtained from solutions containing each of these cations and the nitrite ion was essentially that of the nitrite ion alone. The solutions used were 0.10F in the cation and 0.022F in nitrite ion. Zinc and mercury, however, gave strong evidence of complex formation. A systematic, quantitative study of these complexes would be of considerable interest but has not been undertaken here. Such a study must account satisfactorily for equilibria involving the chloride or other anion complexes and would undoubtedly be of importance.

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